

D3

(10)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 392 320  
A2

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90106362.8

(51) Int. Cl.<sup>5</sup>: A61K 7/06, A61K 7/075,  
C11D 1/88

(22) Date of filing: 03.04.90

(30) Priority: 14.04.89 JP 94495/89

(43) Date of publication of application:  
17.10.90 Bulletin 90/42(94) Designated Contracting States:  
AT CH DE ES FR GB LI NL(71) Applicant: KAO CORPORATION  
1-14-10, Nihonbashikayaba-cho  
Chuo-ku Tokyo(JP)(72) Inventor: Yamashina, Sahoko  
2-9-97 Tomatsuri  
Utsunomiya-shi, Tochigi(JP)  
Inventor: Kumagai, Seichi  
3-20-1 Innai  
Funabashi-shi, Chiba(JP)  
Inventor: Yahagi, Kazuyuki  
6-1-6-749 Ojima  
Koto-ku, Tokyo(JP)(74) Representative: Wächtershäuser, Günter, Dr.  
Tal 29  
D-8000 München 2(DE)

## (54) Shampoo composition.

(57) A shampoo composition is disclosed. The composition comprises an amidoamine-type amphoteric surface active agent, a specific type of modified silicone polymeric compound, and a specific type of polymer. It gives an excellent soft and smooth feeling during washing and rinsing, a superb natural hair-set effect without oily stickiness and roughness, and easy passage of comb through the hair. It is also mild to the skin, the mucous of the eyes, and the like.

EP 0 392 320 A2

EP 0 392 320 A2

## SHAMPOO COMPOSITION

BACKGROUND OF THE INVENTION5 Field of the Invention:

This invention relates to a shampoo composition, and, more particularly, to a shampoo composition comprising an amidoamine-type amphoteric surface active agent, a specific type of modified silicone polymeric compound, and a specific type of polymer. The shampoo composition gives an excellent soft and  
10 smooth feeling during washing and rinsing, a superb natural hair-set effect without oily stickiness and roughness, and easy passage of comb through the hair. It is mild to the skin and the mucous of the eyes and the like.

15 Description of the Background Art:

Conventionally, anionic surfactants such as alkyl sulfates, polyoxyethylenealkyl sulfates, alkylbenzene sulfonates,  $\alpha$ -olefin sulfonates, and the like have widely been used as surfactants for shampoos. These surfactants, however, are more or less irritative to the skin, and roughen the skin if continuously used. On  
20 the other hand, amidoamine-type amphoteric surface active agents are known to be very mild surfactants which give only a little irritation to the skin. More recently, amidoamine-type amphoteric surface active agents having a wider applicability such as those disclosed in Japanese Patent Application Laid-open No. 128100/1988 are used as the base components of shampoos instead of anionic surfactants.

If, however, an addition of a conventional cationic polymer to a shampoo containing an amidoamine-type amphoteric surface active agent as a base component in order to promote its conditioning effect causes unfavorable stickiness when the hair is being dried resulting in starchy, stiff hair due to solid complexes produced by the cationic polymer and the surface active agent. Thus, an addition of a cationic polymer does not give a favorable feeling to the hair after drying, although it can promote light wet feeling and softness. Japanese Patent Application Laid-open Nos. 45406/1981, 74602/1984, 36407/1985, and  
30 56916/1985 disclose shampoo compositions having improved conditioning effects by the addition of silicon-containing cationic polymers, amino-modified organopolysiloxane emulsions, or the like. None of them, however, discloses a shampoo composition imparting low irritation, exhibiting a good conditioning effect, and giving a favorable, natural, dry hair-set. Japanese Patent Application Laid-open No. 307810/1988 discloses a shampoo composition containing an amphoteric surface active agent and an amino-modified  
35 organopolysiloxane emulsion. The advantage of the compound, however, is limited to the conditioning effect after hair washing. Good feeling effects during washing and rinsing cannot be obtained by the simple use of an amino-modified organopolysiloxane emulsion. Japanese Patent Application Laid-open No. 36407 discloses a combined use of a cationic polymer having an amino group or an ammonium group in the main chain and a silicon-containing cationic polymer. The presence of an amino group or an ammonium group in  
40 the main chain of a cationic polymer decreases mutual solubility between the cationic polymer and surface active agents. This produces stiffened hair resulting in poor conditioning effects.

Therefore, development of a shampoo composition which possesses an advantageous feature of amidoamine-type amphoteric surface active agents, while giving an excellent feeling upon use all through washing, rinsing, and drying has been desired.

45 Quality of foam and viscosity are crucial for a shampoo to be a decent commercial product. Shampoos which are superb from the aspect not only of conditioning effects but also of foam quality and usability have been desired.

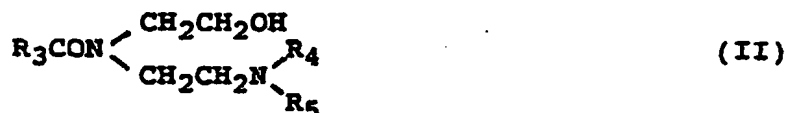
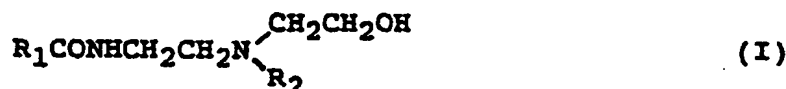
In view of this situation, the present inventors have undertaken extensive studies and have found that a shampoo composition comprising an amidoamine-type amphoteric surface active agent, a specific type of  
50 modified silicone polymeric compound, and a specific type of polymer exhibited improved conditioning effects was mild to the skin and the mucous of the eyes. The inventors further found that when a specific cationic polymer was used as the polymer, the composition exhibited, in addition to the above characteristics, an excellent smooth feeling during washing and rinsing, giving favorable soft finishing. Furthermore, the inventors found that when a specific type of nonionic polymer was used as the polymer, the composition produced fine creamy foam ensuring freely control of viscosity of the shampoo composition.

EP 0 392 320 A2

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a shampoo composition comprising:

(A) one or more amidoamine-type amphoteric surface active agents represented by formula (I) or (II):



wherein  $R_1$  and  $R_3$  each independently represent a saturated or unsaturated hydrocarbon group having 7 to 19 carbon atoms,  $R_2$  and  $R_4$  each independently represent a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  stands for a hydrogen atom, an alkali metal, or an alkanol amine,  $R_5$  represents a hydrogen atom, a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

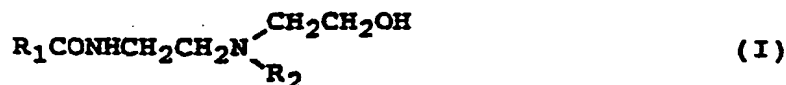
wherein  $M_1$  has the same meaning as defined above,

(B) a modified silicone polymeric compound containing in a molecule at least one aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups, and

(C) one or more compounds selected from water-soluble cationic polymers containing an amino group or an ammonium group which is bonded to the polymer chain and water-soluble cationic polymers containing at least dimethyldiallylammonium halide as its constituent unit.

Another object of the present invention is to provide a shampoo composition comprising:

(A) one or more amidoamine-type amphoteric surface active agents represented by formula (I) or (II):



wherein  $R_1$  and  $R_3$  each independently represent a saturated or unsaturated hydrocarbon group having 7 to 19 carbon atoms,  $R_2$  and  $R_4$  each independently represent a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  stands for a hydrogen atom, an alkali metal, or an alkanol amine,  $R_5$  represents a hydrogen atom, a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  has the same meaning as defined above,

(B) a modified silicone polymeric compound containing in a molecule at least one aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups, and

(D) one or more nonionic polymer.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

EP 0 392 320 A2

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Among amido-amine type amphoteric surface active agents represented by formula (I) or (II), those having linear or branched alkyl or alkenyl groups of C<sub>7</sub> to C<sub>19</sub> for R<sub>1</sub> and R<sub>2</sub>, which generically represent saturated or unsaturated hydrocarbon groups having 7 to 19 carbon atoms, are preferable. Those having linear or branched alkyl groups of C<sub>7</sub> to C<sub>19</sub> for R<sub>1</sub> and R<sub>2</sub> are particularly preferable.

Specific examples of suitable amido-amine type surface active agents represented by the formula (I) include:

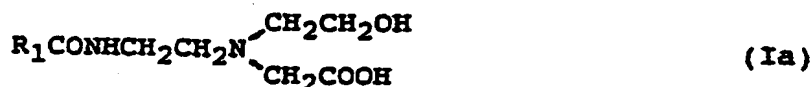
N-lauroyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine, N-lauroyl-N'-carboxyethyl-N'-(2-hydroxyethyl)ethylenediamine, N-myristoyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine, N-myristoyl-N'-carboxyethyl-N'-(2-hydroxyethyl)ethylenediamine, N-palmitoyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine, N-palmitoyl-N'-carboxyethyl-N'-(2-hydroxyethyl)ethylenediamine, and the like as well as their salts. Given as specific examples of suitable amido-amine type surface active agents represented by the formula (IV) are:

N-lauroyl-N-(2-hydroxyethyl)-N'-carboxymethylethylenediamine, N-lauroyl-N-(2-hydroxyethyl)-N',N'-bis(carboxymethyl)ethylenediamine, N-lauroyl-N-(2-hydroxyethyl)-N',N'-bis(carboxyethyl)ethylenediamine, N-myristoyl-N-(2-hydroxyethyl)-N'-carboxymethylethylenediamine, N-myristoyl-N-(2-hydroxyethyl)-N',N'-bis(carboxymethyl)ethylenediamine, N-myristoyl-N-(2-hydroxyethyl)-N',N'-bis(carboxyethyl)ethylenediamine, N-palmitoyl-N-(2-hydroxyethyl)-N'-carboxymethylethylenediamine, N-palmitoyl-N-(2-hydroxyethyl)-N',N'-bis(carboxymethyl)ethylenediamine, N-palmitoyl-N-(2-hydroxyethyl)-N',N'-bis(carboxyethyl)ethylenediamine, and the like as well as their salts.

Given as salts of these compounds are alkali metal salts such as sodium salt, alkali earth metal salt such as magnesium salt, alkanol amine salt such as triethanolamine salt, and the like.

When these types of salts are used, the surface active agent tends to contain inorganic salts as contaminants. It is desirable to use desalted amido-amine type surface active agents from which all or a portion of such inorganic salts is removed so that the content of the inorganic salt contaminants in the final detergent composition be less than 1 % by weight.

Desalted amido-amine type surface active agents can be prepared by solvent extraction, electrodialysis, or the like. A particularly preferable amido-amine type surface active agent can be prepared by converting a secondary amido-amino acid of the following formula (Ia) into a triethanolamine salt and desalting the resulting product to make its salt contaminant concentration 1%.



Such a desalted amido-amine type surface active agent can easily dissolve polymers which are soluble in water but insoluble in concentrated inorganic salt solutions. Here, polymers which are soluble in water but insoluble in concentrated inorganic salt solutions include cationic polymers exhibiting conditioning effects to the skin and hair fibers such as cationic cellulose, cationic starch, cationic natural gums, diallyl quaternary ammonium salt homopolymers, and the like; anionic polymers providing a viscosity increasing effect such as carboxymethyl cellulose, carboxyvinyl polymer, and the like; and nonionic polymers promoting a viscosity increasing effect as well as tactile improvement effect to the skin and the hair such as hydroxyethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, and the like.

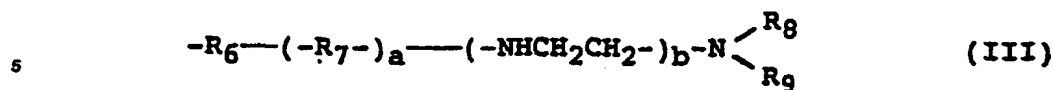
Amido-amine type surface active agents, component (A), can be prepared, for example, by the method described in Japanese Patent Application Laid-open No. 115512/1985. Such amido-amine type surface active agents can be used independently or two or more of them can be used in combination, in an amount of 1-40% by weight, preferably 5-30% by weight, in the composition of the present invention.

Modified silicone polymeric compounds of any molecular structure, e.g. branched, linear, and netting types, can be used as component (B) so long as the same contain in their molecules at least one aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups. Organopolysiloxanes which construct the modified silicone polymeric compounds may include, in addition to the above groups, alkyl groups, e.g. methyl, ethyl, propyl; alkenyl groups, e.g. allyl; aryl groups, e.g. phenyl, naphthyl; cycloalkyl groups, e.g. cyclohexyl; and the like. Those containing methyl group are commonly used.

A typical aminoalkyl group contained in modified silicone polymeric compounds is that shown by the

EP 0 392 320 A2

following formula.



wherein  $R_6$  represents a divalent hydrocarbon group,  $R_7$  represents a group  $-OCH_2CH_2-$ ,



$R_8$  and  $R_9$  are individually a hydrogen or a monovalent hydrocarbon group, and  $a$  and  $b$  denote integers of 1-8.

As divalent hydrocarbon groups represented by  $R_6$ , alkylene groups, e.g. methylene, ethylene, propylene, butylene,  $-CH_2(CH_2)_3CH_2-$ ; and alkylene-arylene groups, e.g.  $-(CH_2)_2-C_6H_4-$ , are given. Of these groups, alkylene groups, particularly propylene group, are preferable. Alkyl groups, e.g. methyl, ethyl, propyl, hexyl; and phenyl group are given as examples of monovalent hydrocarbon groups represented by  $R_8$  and  $R_9$ . Both  $R_8$  and  $R_9$  may be hydrogen atoms, or both may be monovalent hydrocarbon groups, or either one of  $R_8$  and  $R_9$  is a hydrogen, with the other being a monovalent hydrocarbon group. A preferable value for  $a$  and  $b$  is 1.

A typical hydroxyalkyl group which is another group to be contained in the modified silicone polymeric compound molecule is that shown by following formula (IV).



wherein  $-R_6$  has the same meaning as defined above.

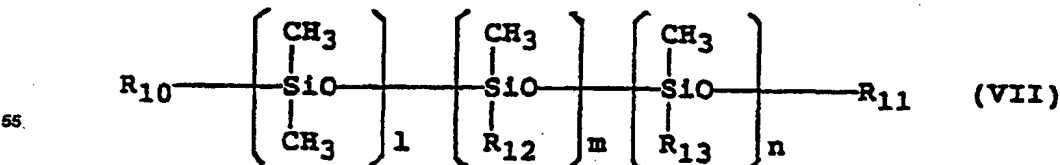
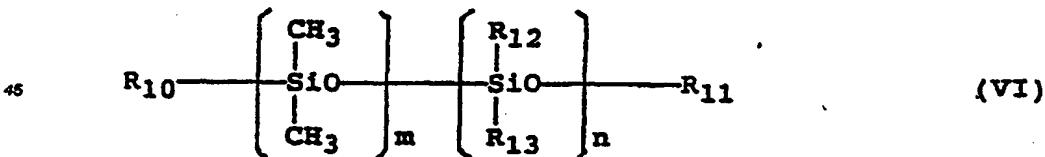
Oxyalkylene and polyoxyalkylene groups are typified by the groups shown by following formula (V).



wherein  $-R_6$  has the same meaning as defined above,  $c$  represent 0 or 1,  $d$  denotes an integer of 1-100, and  $e$  is indicates an integer of 1-5.

Of the hydroxyalkyl groups represented by formula (V), those in which  $c=1$ ,  $d=3$  to 70, and  $e=2$  or 3 are preferable. A hydroxyalkyl group produced by random or block bond of a group having the value  $e=2$  and a group having the value  $e=3$  is acceptable. This applies to the cases where  $e$  is other than 2 or 3.

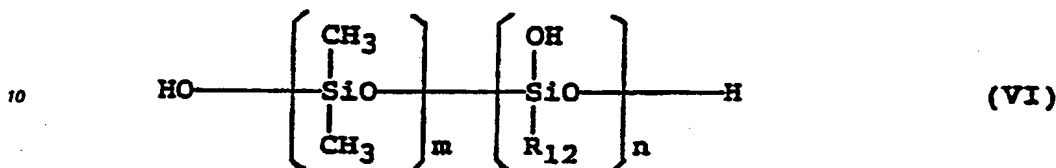
Typical modified silicone polymeric compounds are those represented by formulae (VI) and (VII).



EP 0 392 320 A2

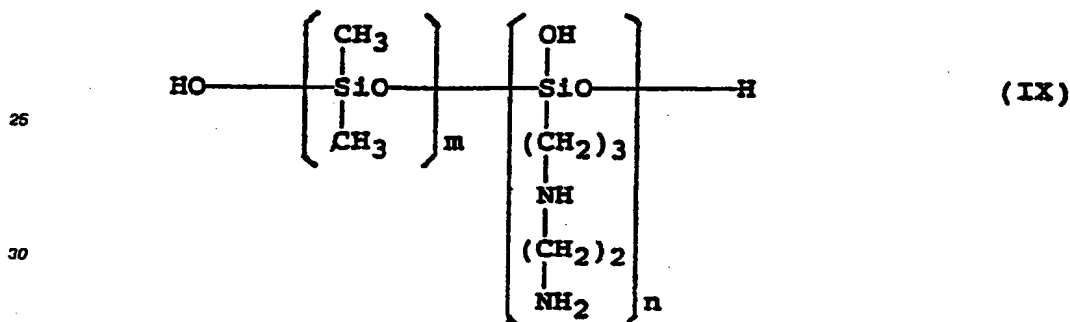
wherein  $R_{10}$  is a methyl or hydroxy group, and  $R_{11}$  is a methyl group or a hydrogen,  $R_{12}$  is above-mentioned aminoalkyl group (III),  $R_{13}$  is a hydroxy, hydroxyalkyl, oxyalkylene, or polyoxyalkylene group, and  $l$ ,  $m$  and  $n$  are integers dependent on the molecular weight.

Of these, particularly preferable modified silicone polymeric compounds are those represented by formula (VIII).



wherein  $R_{12}$  is above-mentioned aminoalkyl group (III), and  $l$ ,  $m$  and  $n$  are integers dependent on the molecular weight.

One of the specific examples of modified silicone polymeric compounds is that described in Cosmetic Ingredient Dictionary, third edition, in the name of Amodimethicone. This is represented by formula (IX) and has average molecular weight of 3,000 to 100,000.



wherein  $m$  and  $n$  are integers dependent on the molecular weight.

It is desirable that the modified silicone polymeric compounds of the present invention be used in a form of aqueous emulsion. Such an emulsion can be obtained by emulsifying, in the presence of a quaternary ammonium salt surfactant and water, a cyclic diorganopolysiloxane and an organodialkoxysilane having an aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups, according to the process described, for example, in Japanese Patent Application Laid-open No. 38609/1981.

When the modified silicone polymeric compounds is used in a form of aqueous emulsion, the amount of modified silicone polymeric compounds in the emulsion is usually 20-60% by weight, and preferably 30-50% by weight.

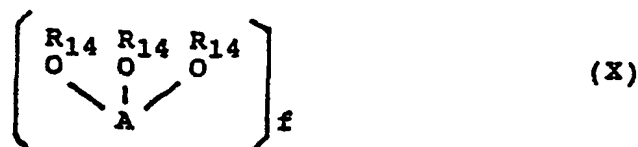
Given as examples of commercial modified silicone polymer emulsions which can be suitably used in this invention are SM 8702C (tradename, product of Toray Silicone Co.) and DC 929 (tradename, product of Dow Corning Co.).

Component (B) is used in an amount of 0.005-0.3% by weight, and preferably 0.01-0.25% by weight, in the composition of the present invention. When component (B) is in a form of an aqueous emulsion, the amount of the aqueous emulsion incorporated into the composition of the present invention is 0.01-0.5% by weight, and preferably 0.05-0.4% by weight.

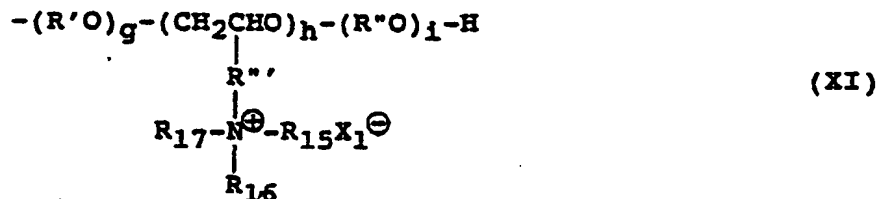
Cationic polymers used in this invention as component (C) are (i) water-soluble polymers containing an amino group or an ammonium group which is bonded to the polymer chain or (ii) water-soluble polymers containing at least dimethyldiallylammonium halide as its constituent unit. Examples of these polymers include cationized cellulose derivatives, cationic starch, cationic natural gums, copolymers of diallyl quaternary ammonium salt and acrylamide, quaternized polyvinylpyrrolidone derivatives, and the like.

A compound of following formula (X) is given as an example of preferred cationized cellulose derivatives:

EP 0 392 320 A2



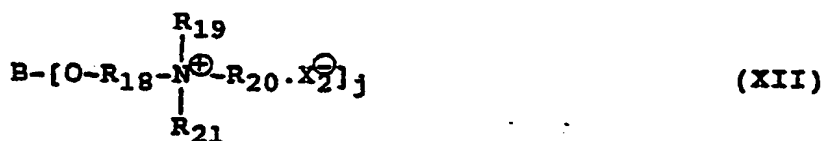
wherein A represents an anhydrous glucose unit residue, f denotes an integer of 50 to 20,000, and each  $R_{14}$  individually represents a group represented by the following formula (XI):



wherein  $R'$  and  $R''$  individually represent an alkylene group having 2 or 3 carbon atoms, g is an integer of 0 to 10, h is an integer of 0 to 3, i is an integer of 0 to 10,  $R''$  represents an alkylene group or a hydroxyalkylene group each having 1 to 3 carbon atoms,  $R_{15}$ ,  $R_{16}$ , and  $R_{17}$  may be the same or different and represent alkyl groups, aryl groups, aralkyl groups, each having not more than 10 carbon atoms, or may form a heterocycle together with the nitrogen atom, and  $X_1$  represents an anion, e.g. chlorine, bromine, iodine, sulfuric acid, sulfonic acid, methyl sulfate, phosphoric acid, nitric acid, and the like.

A preferable range of the cation substitution degree in cationized cellulose is 0.01 to 1, i.e., in terms of the average value of h for anhydrous glucose 0.01 to 1, and preferably 0.02 to 0.5. The average of g plus i is 1 to 3. A substitution degree of below 0.01 is not sufficient. The value not more than 1 is preferable from the aspect of the reaction yield, although the value above 1 can be acceptable. The molecular weight of the cationic cellulose used is between 100,000 and 3,000,000.

The compounds represented by the following formula (XII) are preferable cationic starches.



wherein B represents a starch residual group,  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$ , and  $R_{21}$  may be the same or different and represent alkyl groups, aryl groups, aralkyl groups, each having not more than 10 carbon atoms, or may form a heterocycle together with the nitrogen atom,  $X_2$  represents an anion, e.g. chlorine, bromine, iodine, sulfuric acid, sulfonic acid, methyl sulfate, phosphoric acid, nitric acid, and the like, and j is a positive integer.

A preferable range of the cation substitution degree of cationic starch is 0.01 to 1. Specifically, cationic starches having 0.01 to 1, preferably 0.02 to 0.5, cationic group per anhydrous glucose unit are desirable. A substitution degree of below 0.01 is not sufficient. The value not more than 1 is preferable from the aspect of the reaction yield, although the value above 1 can be acceptable.

A preferable cationized guar-gum derivative is that



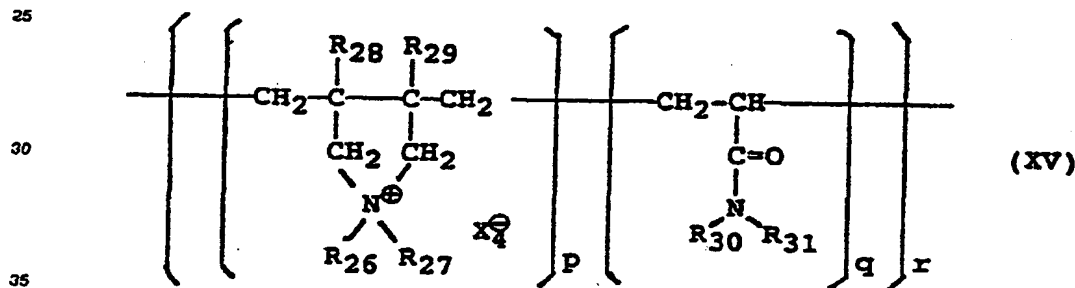
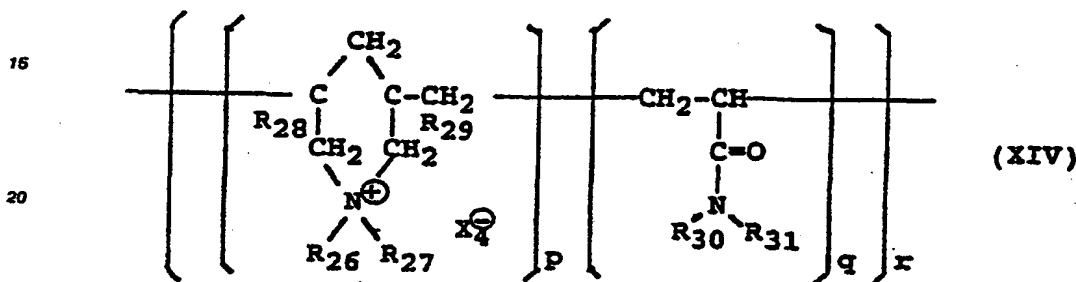
wherein D represents a guar-gum residual group,  $R_{22}$  represents a alkylene group or a hydroxyalkylene

EP 0 392 320 A2

group,  $R_{23}$ ,  $R_{24}$ , and  $R_{25}$  may be the same or different and represent alkyl groups, aryl groups, aralkyl groups, each having not more than 10 carbon atoms, or may form a heterocycle together with the nitrogen atom,  $X_3$  represents an anion, e.g. chlorine, bromine, iodine, sulfuric acid, sulfonic acid, methyl sulfate, phosphoric acid, nitric acid, and the like, and  $k$  is a positive integer.

5 A preferable range of the cation substitution degree of cationic starch is 0.01 to 1. Specifically, cationic guar-gum derivatives having 0.01 to 1, preferably 0.02 to 0.5, cationic group per sugar unit are desirable. This type of cationic polymers is described in Japanese Patent Publication Nos. 35640/1983 and 46158/1985, and Japanese Patent Application Laid-open No. 53996/1983, and is commercially available in the tradename of Jagual (product of Cellanase Stein-Hohl Co.).

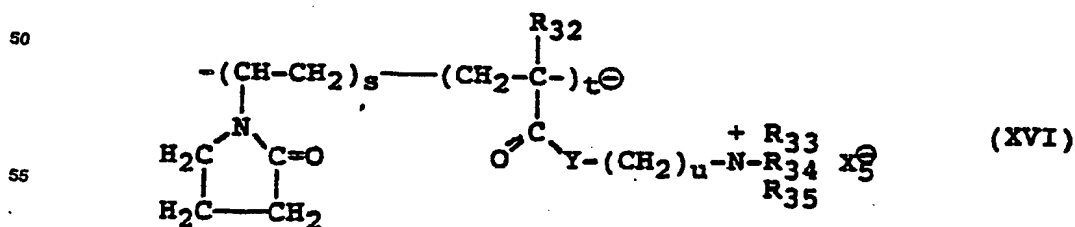
10 The compounds represented by the following formula (VIII) or (IX) are preferable as a cationic diallyl quaternary ammonium salt/acryl amide copolymer.



wherein  $R_{26}$  and  $R_{27}$  may be the same or different and represent hydrogen atoms, alkyl groups having 1 to 18 carbon atoms, phenyl groups, hydroxyalkyl groups, amidealkyl groups, cyanoalkyl groups, alkoxyalkyl groups, or carboalkoxyalkyl groups,  $R_{28}$ ,  $R_{29}$ ,  $R_{30}$ , and  $R_{31}$  may be the same or different and represent hydrogen atoms, lower alkyl groups having 1 to 3 carbon atoms, or phenyl groups,  $X_4$  represents an anion, e.g. chlorine, bromine, iodine, sulfuric acid, sulfonic acid, methyl sulfate, nitric acid, and the like,  $p$  is an integer of 1 to 50,  $q$  is an integer of 1 to 50, and  $r$  is an integer of 150 to 8,000.

45 The molecular weight of a diallyl quaternary ammonium salt/acryl amide copolymer is in the range of 30,000 to 2,000,000, and preferably of 100,000 to 1,000,000.

Compounds represented by the following formula (XVI) are preferable as a quaternized polyvinylpyrrolidone derivative.





## EP 0 392 320 A2

wherein  $R_{32}$  represents a hydrogen atom or a lower alkyl group having 1 to 3 carbon atoms,  $R_{33}$ ,  $R_{34}$ , and  $R_{35}$  may be the same or different and represent hydrogen atoms, alkyl groups having 1 to 4 carbon atoms, hydroxyalkyl groups, amidealkyl groups, cyanoalkyl groups, alkoxyalkyl groups, or carboalkoxyalkyl groups, Y represents an oxygen atom or the NH group of an amide bond,  $X_5$  represents an anion, e.g. chlorine, bromine, iodine, sulfuric acid, sulfonic acid, alkyl sulfate of a  $C_{1-4}$  carbon atom content, phosphoric acid, nitric acid, and the like, u is an integer of 1 to 10, s and t are integers satisfying  $s + t = 20$  to 8,000.

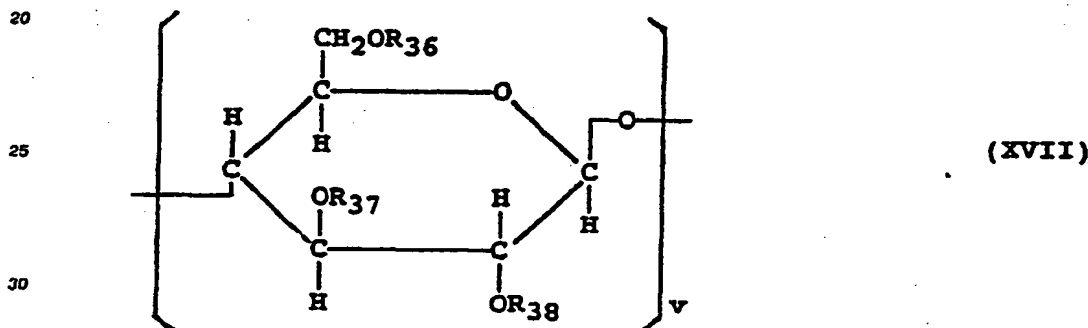
A molecular weight of a quaternarized polyvinylpyrrolidone derivative is between 10,000 and 2,000,000, with the particularly preferable range being between 50,000 and 1,500,000.

The content of the cationic nitrogen originating from cationic polymers in the above vinyl polymers is 0.004 to 0.2%, and preferably 0.01 to 0.15% of the vinyl polymers. A sufficient effect cannot be expected from the nitrogen atom content of less than 0.004%. On the other hand, the content of above 0.2% causes the vinyl polymer becoming colored and is disadvantageous in view of economy, even though a good performance can be obtained.

The above cationic polymers are incorporated into the composition of the present invention as component C either independently or in combination in an amount of 0.01 to 2% by weight, and preferably 0.1 to 0.8% by weight.

Following examples are given as preferable nonionic polymer, component (D), of the present invention.

(1) Cellulose derivatives



wherein  $R_{36}$ ,  $R_{37}$ , and  $R_{38}$  may be the same or different and represent a hydrogen atom, a group  $-(CH_2CH_2O)_w-$ , wherein w is a number 1-5,  $-CH_3$ , or  $-C_2H_5OH$ ; and v is a number 50-500.

Specific examples include hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, and the like.

Of these, hydroxyethyl cellulose are commercially available in the tradenames of Cellosize (product of UCC), Natrosol (product of Hercules Corp.), and the like. For the purpose of the present invention those having 1.0-4.0, preferably 1.8-3.0, moles of ethylene oxide added per glucose residue are suitable.

Other commercially available products are Viscontran MC (methyl cellulose, product of Henkel Co.), Klucel (hydroxypropyl cellulose, product of Hercules Corp.), Metholose (hydroxypropylmethyl cellulose, product of Shinetsu Chemical Co.), Viscontran MHPC (hydroxypropylmethyl cellulose, product of Henkel Co.), and the like. In these methyl cellulose, those containing 10-40%, preferably 20-30%, of methoxy group and 1-20%, preferably 5-15%, of hydropropoxy group are suitable.

(2) Polyvinyl alcohol derivatives

(3) Polyvinylalkyl ether derivatives

(4) Polyethylene oxide derivatives

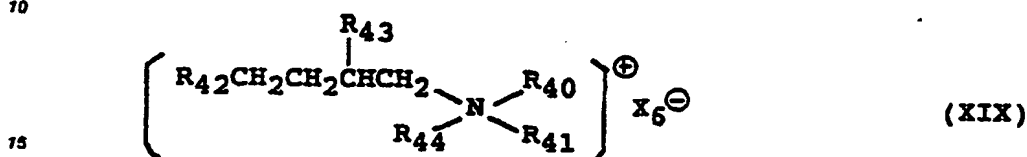
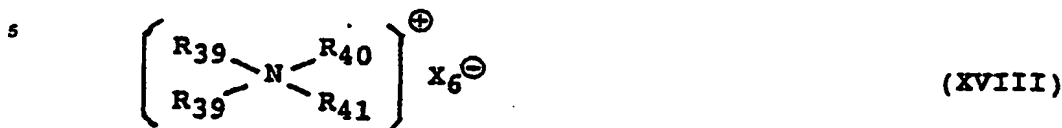
The above nonionic polymers are incorporated into the composition of the present invention as component D either independently or in combination in an amount of 0.01 to 3% by weight, and preferably 0.1 to 2% by weight.

The shampoo composition of the present invention can be prepared according to a conventional method by using components (A), (B), and (C), or components (A), (B), and (D). Both types exhibit an excellent conditioning effect and are only slight irritative. When the cationic polymer of component (C) is used, the composition gives exceptionally good feeling during washing and rinsing, and softly finished hair after drying. When the nonionic polymer of component (D) is used, the composition which can produce creamy foam can be obtained. Viscosity of shampoos can be freely controlled by using such a composition.

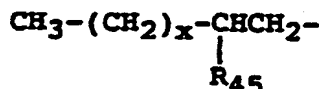
When one or more quaternary branched ammonium salts represented by following formula (XVIII) or

EP 0 392 320 A2

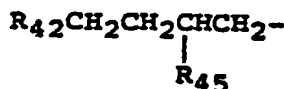
(XIX) are used together with the above components, the composition exhibits improved softness and smoothness, as well as even better conditioning effects.



wherein  $R_{39}$  represents a mixture of (a) a branched alkyl group represented by



and (b) a linear alkyl group represented by  $CH_3-(CH_2)_y-$  (wherein  $R_{45}$  represents a methyl or ethyl group,  $x$  is an integer to make the carbon atom content of the branched alkyl group 8 to 16, and  $y$  is an integer of 7 to 15), with a ratio (a)/(a) + (b) being 0.1 to 1,  $R_{40}$  and  $R_{41}$  independently represent a benzyl group, an alkyl group having 1 to 3 carbon atoms, or a hydroxyalkyl group having 1 to 3 carbon atoms,  $R_{42}$  and  $R_{43}$  independently represent an alkyl group having 2 to 12 carbon atoms,  $R_{44}$  represents a group



or an alkyl group having 1 to 3 carbon atoms, and  $X_6^-$  represents a halogen ion or an organic anion.

Specific examples of particularly preferable branched quaternary ammonium salts represented by formula (XVIII) are dialkyldimethylammonium chloride in which the alkyl group  $R_{39}$  has 8 to 16 carbon atoms and a branched ratio is 0.1 to 0.5. Given as preferable examples of this branched quaternary ammonium salt of formula (XIX) are 2-decyltetradecyltrimethylammonium chloride, 2-dodecylhexadecyltrimethylammonium chloride, di-2-hexyldecyldimethylammonium chloride, di-2-octyldodecylammonium chloride, and the like.

Besides the above two essential components, various components commonly known for use in a shampoo composition can be formulated to the extent that the effects of the present invention is not adversely affected. Such optional components include, for example, foaming promoters, e.g. anionic, amphoteric, and nonionic surface active agents; tactile improvers, e.g. salts of higher fatty acid, alkylamine oxides, fatty acid alkanol amide, squalane, lanoline; moisturizing agents, e.g. propylene glycol, glycerin, diethylene glycol, monoethyl ether, sorbitol; viscosity adjustment agents, e.g. methyl cellulose, carboxyvinyl polymer, hydroxyethyl cellulose, polyoxyethylene glycol distearate, ethanol; pearling agents, perfumes, coloring agents, UV absorbers, antioxidants, antiseptics, e.g. triclosan, trichlorocarbanilide; anti-inflammation agents, e.g. potassium glytylphosphate, tochopheryl acetate; antidandruff agents, e.g. zinc pyrition, octopirox; preservatives, e.g. methyl paraben, butyl paraben; and the like.

The problems due to secondary amidoamino acids and their salts in shampoo compositions, i.e., poor conditioning effects, such as uneasy finger passage through the hair both in dry and wet conditions and poor feeling to the touch, have been improved by the present invention. Furthermore, the composition of the present invention provides foam with improved quality and makes viscosity control easy. It can be directed to products requiring lower irritation to the skin and the mucosa, e.g. shampoos for babies, for persons

EP 0 392 320 A2

having delicate, sensitive skin, for people who frequently wash hair, and the like. It can also suitably be used for the hair suffering from bad finger or comb passage due to perm treatment, for the hair which can be set only with difficulty.

Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

### EXAMPLES

#### Example 1

Shampoo compositions were prepared according to the formulations listed in Tables 1 to 3. Each composition was tested in terms of its feeling (sensory evaluation) and the irritation to the skin, during washing, rinsing, after drying with towel, after air-drying.

In the sensory evaluation, 1 g of sample composition was applied to a bundle of hair (weight: 20 g, length: 15 cm) of a healthy Japanese woman. Feeling to the touch when the shampoo was foamed for 1 minute; finger passage through the hair during rinsing; finger passage through the hair and stickiness after drying with towel; and stickiness, hair-set easiness, and passage of comb through the hair after drying with dryer were evaluated by 5 expert panelists according to the following standards. The irritation to the skin was evaluated by washing the skin of guinea pigs seven times with a 25% solution of the shampoo composition. Shampoo compositions to which a nonionic polymer was added were also evaluated with respect to the solubility of the polymer and the quality of the foam.

#### <Evaluation Standard>

##### Feeling to the touch during washing:

AAA: Soft and smooth, fingers pass through very easily

BBB: Smooth, fingers pass through easily

CCC: Hair is not slippery, fingers pass through with difficulty

DDD: Hair feels creaky and tangles

##### Passage of finger through the hair:

AAA: Hair gives no creaky feeling at all, fingers pass through very easily

BBB: Hair gives only slight creaky feeling, fingers pass through easily

CCC: Hair gives rather strong creaky feeling, fingers pass through with difficulty

DDD: Hair gives strong creaky feeling, fingers do not pass through easily

##### Stickiness:

AAA: Hair is not sticky but sleek

BBB: Hair is slightly sticky

CCC: Hair is sticky

##### Softness:

AAA: Hair is very soft and pliable

BBB: Hair is soft

CCC: Hair is a little devoid softness

DDD: Hair is stiff

##### Hair-setup performance:

EP 0 392 320 A2

AAA: Hair is naturally setup  
BBB: Setup is not always complete  
CCC: Setup is incomplete with many hair-flies

## 5 Passage of comb:

AAA: Hair is smooth providing good passage of comb  
BBB: Comb passage is slightly braked  
CCC: Comb does not easily go through the hair

10

## Irritation to the skin:

AAA: Irritation is very low  
BBB: Slightly irritative  
CCC: Irritation is rather strong

15

## Solubility of nonionic polymer:

AAA: 1% of nonionic polymer added makes a transparent solution at room temperature  
BBB: 1% of nonionic polymer added resulted in a slightly turbid solution at room temperature  
CCC: 1% of nonionic polymer added resulted in a turbid solution or formed precipitate at room temperature

20

## Quality of foam:

AAA: Foam is creamy  
BBB: Foam is slightly creamy  
BBB: Foam is rough

25

30

35

40

45

50

55

EP 0 392 320 A2

TABLE 1

	Comparative Compositions						Invention Compositions					
	1	2	3	4	1	2	3	4	5	6		
Sodium N-lauryl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine	15	-	15	-	15	-	15	15	15	15		15
Sodium N-lauryl-N-(2-hydroxyethyl)-N',N'-bis(carboxymethyl)ethylenediamine	-	15	-	15	-	15	-	-	-	-		-
Cationized polymer #1	-	-	1.0	1.0	0.5	0.5	0.5	0.5	0.5	0.5		0.5
Modified silicone aqueous emulsion #2	-	-	-	-	0.1	0.1	0.01	0.05	0.4	0.5		0.5
Purified water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance		Balance

EP 0 392 320 A2

TABLE 1 (Continued)

	Comparative Compositions						Invention Compositions					
	1	2	3	4	1	2	3	4	5	6		
Feeling during washing	DDO	DDO	BBB	BBB	AAA	AAA	BBB	BBB	AAA	AAA		
Finger passage during rinsing	DDO	DDO	AAA	AAA	AAA	AAA	BBB	BBB	AAA	AAA		
Finger passage after drying with towel	DDO	DDO	BBB	BBB	AAA	AAA	BBB	BBB	AAA	AAA		
Stickiness after drying with towel	AAA	AAA	CCC	CCC	AAA	AAA	AAA	AAA	AAA	AAA		
Stickiness after drying with dryer	AAA	AAA	CCC	CCC	AAA	AAA	AAA	AAA	AAA	AAA		
Hair-set after drying with dryer	CCC	CCC	BBB	BBB	AAA	AAA	AAA	AAA	AAA	AAA		
Comb passage after drying with dryer	CCC	CCC	BBB	BBB	AAA	AAA	AAA	AAA	AAA	AAA		
Irritation to the skin	AAA	AAA	AAA	AAA	AAA	AAA	AAA	AAA	AAA	AAA		

\*1 Polymer JM-400 (Tradename: cationized cellulose, product of UCC)

\*2 DC 928 (Tradename: modified silicone polymer, containing 35% Amodimethicone, product of Dow Corning.

EP 0 392 320 A2

TABLE 2

5		Invention Compositions				
		7	8	9	10	11
10	N-lauroyl-N'-carboxy-methyl-N'-(2-hydroxy-ethyl)ethylenediamine triethanolamine	18	18	18	18	18
	Cationized polymer 1 *1	0.1	0.5	-	-	-
15	Cationized polymer 2 *2	-	-	0.5	-	-
	Cationized polymer 3 *3	-	-	-	0.5	-
	Cationized polymer 4 *4	-	-	-	-	0.5
20	Modified silicone aqueous emulsion *5	0.3	0.3	0.3	0.3	0.3
	Purified water	Balance	Balance	Balance	Balance	Balance

25

30

35

40

45

50

55

EP 0 392 320 A2

TABLE 2 (Continued)

5		Invention Compositions				
		7	8	9	10	11
10	Feeling during washing	AAA	AAA	AAA	AAA	AAA
	Finger passage during rinsing	AAA	AAA	AAA	AAA	AAA
15	Finger passage after drying with towel	AAA	AAA	AAA	AAA	AAA
	Stickiness after drying with towel	AAA	AAA	AAA	AAA	AAA
20	Softness after drying with towel	BBB	AAA	AAA	AAA	AAA
	Stickiness after drying with dryer	AAA	AAA	AAA	AAA	AAA
25	Hair-set after drying with dryer	AAA	AAA	AAA	AAA	AAA
	Comb passage after drying with dryer	AAA	AAA	AAA	AAA	AAA
30	Irritation to the skin	AAA	AAA	AAA	AAA	AAA

35

\*1 Polymer JR-400 (Tradename: cationized cellulose, product of UCC)

\*2 Cationized corn starch, cationized degree: 0.3

40

\*3 Marcoat 550 (Tradename: copolymer of N,N-dimethyl-3,5-methylene-piperidinium chloride and acrylamide, product of Merck Co.)

45

\*4 Gafcoat 755N (Tradename: quarternarized ethyl sulfate of vinyl-pyrrolidone dimethylaminoacrylate copolymer, product of Guff Corp.)

50

\*5 DC 929 (Tradename: modified silicone polymer, containing 35% Amodimethicone, product of Dow Corning).

55



EP 0 392 320 A2

TABLE 3

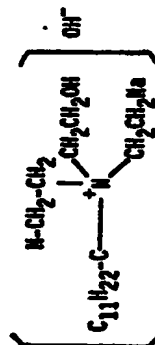
	Comparative Compositions					Invention Compositions						
	5	6	7	12	13	14	15	16	17			
2-Lauryl-N-carboxymethyl-N-hydroxymethylimidazolium betaine *1	18	18	-	-	-	-	-	-	-			
N-lauryl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine triethanolamine	-	-	18	18	18	18	18	18	18			
Nonionic polymer *2	0.8	-	-	-	-	-	-	2.0	0.5			
Nonionic polymer *3	-	0.5	-	0.1	0.2	0.8	2.0	-	-			
Modified silicone aqueous emulsion *4	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2			
Purified water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance			

EP 0 392 320 A2

TABLE 3 (Cont inued)

	Comparative Compositions					Invention Compositions						
	5	6	7	12	13	14	15	16	17			
Feeling during washing	BBB	BBB	BBB	BBB	BBB	BBB	BBB	BBB	BBB			
Quality of foam	BBB	BBB	CCC	AAA	AAA	AAA	AAA	AAA	AAA			
Irritation to the skin	AAA	AAA	AAA	AAA	AAA	AAA	AAA	AAA	AAA			
Solubility of polymer	CCC	CCC	-	AAA	AAA	AAA	AAA	AAA	AAA			

\*1 Softazolin CH: Tradename, compound having the following structure manufactured by Kawaken Fine Chemical Co.



\*2 Metholose 60SH50 (product of Shin-etsu Chemical Co.)

\*3 LA-18 (polyvinyl alcohol, product of Shin-etsu Chemical Co.)

\*4 SH 8702C (Tradename: modified silicone polymer, containing 40% Acodimethicone, product of Toray Silicone Co.)

As evidenced by the above evaluation results, the shampoo composition of the present invention exhibits excellent passage of finger through the hair under both wet and dry conditions, superb feeling upon use, good hair-set effects. The composition dissolves ionic polymers well and produced foam with good quality. Its viscosity can easily be controlled.

#### Examples 2-4

All shampoo compositions having formulations of Examples 2-4 were very mild to the skin with little irritation and exhibited excellent conditioning effects.

EP 0 392 320 A2

Example 2	
	% by weight
Ammonium N-lauroyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine	12
Sodium polyoxyethylene(EO = 3.0) lauryl ether sulfate	5
Lauric acid diethanolamide	3
Cationic polymer (Marcoat 100, Merck Co.)	0.2
Modified silicone aqueous suspension (SM 8702C, Toray Silicone Co.)	0.07
Antiseptic	0.1
Perfume, Colorant	Appropriate amount
Water	Balance

Example 3	
	% by weight
N-lauroyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine triethanolamine	18
Lauryldimethylaminoacetic acid betaine	3
2-Decyltetradecyltrimethylammonium chloride	0.3
Modified silicone aqueous suspension (DC-929, Dow Corning Co.)	0.05
Metholose 60SH400 (Shin-etsu Chemical Co.)	1.0
Antiseptic	0.1
Perfume, Colorant	Appropriate amount
Water	Balance

Example 4	
	% by weight
N-lauroyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine triethanolamine	15
Laurylamine oxide	5
Cationic polymer (Polymer JR-400, product of UCC)	0.2
Py lactoneohramine (octopirox)	1.0
Modified silicone aqueous suspension (SM 8702C, Toray Silicone Co.)	0.2
Polyvinyl alcohol	0.5
Laurylamidopropyldimethylaminoacetic acid betaine	1.0
Antiseptic	0.1
Perfume, Colorant	Appropriate amount
Water	Balance

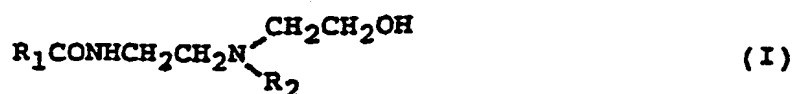
Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

#### Claims

1. A shampoo composition comprising:

(A) one or more amidoamine-type amphoteric surface active agents represented by formula (I) or (II):

EP 0 392 320 A2



wherein  $R_1$  and  $R_3$  each independently represent a saturated or unsaturated hydrocarbon group having 7 to 19 carbon atoms,  $R_2$  and  $R_4$  each independently represent a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  stands for a hydrogen atom, an alkali metal, or an alkanol amine,  $R_5$  represents a hydrogen atom, a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

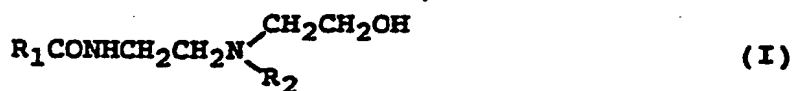
wherein  $M_1$  has the same meaning as defined above,

(B) a modified silicone polymeric compound containing in a molecule thereof at least one aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups, and

(C) one or more compounds selected from water-soluble cationic polymers containing an amino group or an ammonium group which is bonded to the polymer chain and water-soluble cationic polymers containing at least dimethyldiallylammonium halide as its constituent unit.

2. A shampoo composition comprising:

(A) one or more amidoamine-type amphoteric surface active agents represented by formula (I) or (II):



wherein  $R_1$  and  $R_3$  each independently represent a saturated or unsaturated hydrocarbon group having 7 to 19 carbon atoms,  $R_2$  and  $R_4$  each independently represent a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  stands for a hydrogen atom, an alkali metal, or an alkanol amine,  $R_5$  represents a hydrogen atom, a group  $-\text{CH}_2\text{COOM}_1$ ,  $-\text{CH}_2\text{CH}_2\text{COOM}_1$ , or  $-\text{CH}_2 \begin{array}{c} \text{CHCH}_2\text{SO}_3\text{M}_1 \\ | \\ \text{OH} \end{array}$ ,

wherein  $M_1$  has the same meaning as defined above,

(B) a modified silicone polymeric compound containing in a molecule thereof at least one aminoalkyl group and at least one group selected from hydroxyl, hydroxyalkyl, oxyalkylene, and polyoxyalkylene groups, and

(D) one or more nonionic polymer.

⑬



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number:

**0 392 320 A3**

⑫

**EUROPEAN PATENT APPLICATION**

① Application number: 90106362.8

⑤ Int. Cl.<sup>5</sup>: **A61K 7/06, A61K 7/075,  
C11D 1/88**

② Date of filing: 03.04.90

③ Priority: 14.04.89 JP 94495/89

④ Date of publication of application:  
17.10.90 Bulletin 90/42⑥ Designated Contracting States:  
**AT CH DE ES FR GB LI NL**⑧ Date of deferred publication of the search report:  
04.03.92 Bulletin 92/10⑦ Applicant: **KAO CORPORATION**  
**1-14-10, Nihonbashikayaba-cho**  
**Chuo-ku Tokyo(JP)**⑨ Inventor: **Yamashina, Sahoko**  
**2-9-97 Tomatsuri**  
**Utsunomiya-shi, Tochigi(JP)**  
Inventor: **Kumagai, Seichi**  
**3-20-1 Innai**  
**Funabashi-shi, Chiba(JP)**  
Inventor: **Yahagi, Kazuyuki**  
**6-1-6-749 Ojima**  
**Koto-ku, Tokyo(JP)**⑩ Representative: **Wächtershäuser, Günter, Dr.**  
**Tal 29**  
**W-8000 München 2(DE)**

⑭ Shampoo composition.

⑮ A shampoo composition is disclosed. The composition comprises an amidoamine-type amphoteric surface active agent, a specific type of modified silicone polymeric compound, and a specific type of polymer. It gives an excellent soft and smooth feeling during washing and rinsing, a superb natural hair-set effect without oily stickiness and roughness, and easy passage of comb through the hair. It is also mild to the skin, the mucous of the eyes, and the like.

EP 0 392 320 A3



European  
Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 10 6362

## DOCUMENTS CONSIDERED TO BE RELEVANT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y,D	EP-A-0 269 939 (KAO CORPORATION) " the whole document " - - -	1-2	A 61 K 7/06 A 61 K 7/075 C 11 D 1/88
Y,D	GB-A-2 058 103 (BRISTOL-MYERS COMPANY) " the whole document " - - -	1-2	
A	EP-A-0 078 597 (TORAY SILICONE COMPANY LIMITED) " the whole document " - - -	1-2	
A	DE-A-2 752 116 (THE LION FAT AND OIL CO., LTD.) " claims 1-15 " - - -	1-2	
A	GB-A-2 165 550 (L'OREAL) " the whole document " - - - - -	1-2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 61 K
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
Berlin		20 December 91	SIATOU E
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date	
Y: particularly relevant if combined with another document of the same category		D: document cited in the application	
A: technological background		L: document cited for other reasons	
O: non-written disclosure			
P: intermediate document			
T: theory or principle underlying the invention		&: member of the same patent family, corresponding document	